

# On the validity of the Onsager relations in relativistic binary mixtures

Valdemar Moratto<sup>1</sup>, A. L. Garcia-Perciante<sup>2</sup>, L. S. Garcia-Colin<sup>1 and 3</sup>

<sup>1</sup>*Depto. de Fisica, Universidad Autonoma Metropolitana-Iztapalapa,  
Av. Purisima y Michoacan S/N, Mexico D. F. 09340, Mexico.*

<sup>2</sup>*Depto. de Matematicas Aplicadas y Sistemas,  
Universidad Autonoma Metropolitana-Cuajimalpa,  
Artificios 40 Mexico D.F 01120, Mexico. and*

<sup>3</sup>*El Colegio Nacional,  
Luis Gonzalez Obregon 23, Centro Historico,  
Mexico D. F. 06020, Mexico.*

## Abstract

In this work we study the properties of a relativistic mixture of two non-reacting dilute species in thermal local equilibrium. Following the conventional ideas in kinetic theory, we use the concept of chaotic velocity. In particular, we address the nature of the density, or pressure gradient term that arises in the solution of the linearized Boltzmann equation in this context. Such effect, also present for the single component problem, has so far not been analyzed from the point of view of the Onsager reciprocity relations. In order to address this matter, we propose two alternatives for the Onsagerian matrix which comply with the corresponding reciprocity relations and also show that, as in the non-relativistic case, the chemical potential is not an adequate thermodynamic force. The implications of both representations are briefly analyzed.

PACS: 05.20.Dd, 03.30.+p, 05.70.Ln.

## I. INTRODUCTION

Relativistic kinetic theory has become a rather fashionable subject in recent years. Not only this is due to many astrophysical and cosmological phenomena which occur in dilute gases at high temperatures, but also because for a while, it was believed it would find an important application in the study of the quark gluon plasma which is formed in relativistic heavy ion collisions (RHIC). Although this last feature is questionable [1–3] mostly because a relativistic quantum hydrodynamical theory is required, interest still remains due to its applications to classical systems.

It is our view that in spite of the existence of the wealth of approaches to this classical problem, which goes back to Israel et. al. [4–7], there are two aspects that have been so far ignored in previous works. First, the formulation of the theory using the rather useful concept of chaotic (thermal) velocities of the molecules composing the gas. Secondly, the study of the so called cross effects in irreversible thermodynamics. Also, and even more important, the possibility of selecting appropriate representations of fluxes and their conjugate forces in which one can provide an airtight-proof on the validity of Onsager’s reciprocity relations (ORR) has to our knowledge, never been given. It is important to emphasize at this point that the validity of the ORR is one of the fundamental postulates of Linear Irreversible Thermodynamics (LIT).

The introduction of the concept of thermal velocity has been successfully accomplished for a single component dilute gas and its advantages clearly underlined in the calculation of their transport properties [8, 9]. Perhaps it is worth stressing that in this formulation the relativistic generalization of the classical expression for the heat flux obtained emphasizes the nature of heat namely, the transport of the kinetic or thermal energy of the molecules. Further, one can obtain in a rigorous way the expression for the relativistic stress tensor as proposed phenomenologically by C. Eckart in 1940 [10].

In this paper we study the second feature as mentioned above, the cross effects and the validity of the ORR in a binary non-reactive diluted mixture of gases. The most surprising result is that there are two representations in which the ORR hold true, depending on how fluxes and forces are selected. One of the representations follows the idea formulated by previous authors of coupling in one single force both the temperature and pressure gradients, this force being the direct drive

for the heat flux. The ORR are verified in that context. The second one is based on the novel idea that due to the non-invariance of the volume elements of the gas under Lorentz transformations, a “volume flux” results whose conjugate force is the pressure gradient. Resemblance to this idea arose in at least one phenomenological derivation of Burnett’s constitutive equations and has also been subject of reformulations of classical hydrodynamics [11–13]. Further, two new cross effects are present in this approach which are completely absent in the non-relativistic case.

To accomplish this task, we divide the article as follows: Section 2 is devoted to the basic concepts of the relativistic kinetic theory, as well as the derivation of the conservation equations. In section 3 we use the Chapman-Enskog method to linearize the Boltzmann equation. In section 4 we select the appropriate thermodynamic forces following the ideas in Refs. [6, 7], and we show that the Onsager reciprocity relations [14–16] in a  $2 \times 2$  matrix hold. In section 5 we propose the new idea of a new purely relativistic flux directly coupled with the pressure gradient, which satisfies the symmetry of a  $3 \times 3$  “Onsagerian” matrix and further, we show that the chemical potential in this context is not an appropriate thermodynamic force. Finally, in section 6, we include a discussion and concluding remarks.

## II. RELATIVISTIC KINETIC THEORY

As mentioned above, we study a relativistic, dilute mixture of two non-reacting species in thermal local equilibrium. In the framework of kinetic theory, we consider the quantity

$$f_{(1)} d^3x d^3v_{(1)} + f_{(2)} d^3x d^3v_{(2)} \quad (\text{II.1})$$

which represents the number of particles of species (1) and (2) in  $d^3x d^3v_{(1)}$  and  $d^3x d^3v_{(2)}$ , where  $v_{(i)}^\alpha$  denotes molecular velocity. To establish a clear notation, we use parenthesis in the subscripts to denote species. For components, Latin subscripts run from 1 to 3 for the spatial ones while Greek subscripts are used for four-vectors and tensors running from 1 to 4 in Minkowski’s space-time with a  $+++ -$  signature.

The invariant Boltzmann equations for the mixture are,

$$v_{(i)}^\alpha f_{(i),\alpha} = \sum_{j=1}^2 J_{(ij)} \quad (\text{II.2})$$

where the collisional term is given by [7],

$$\sum_{i,j=1}^2 J_{(ij)} = \sum_{i,j=1}^2 \int (f'_{(i)} f'_{(j)} - f_{(i)} f_{(j)}) F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 v_{(j)}^*. \quad (\text{II.3})$$

Here,  $F_{(ij)}$ ,  $\sigma_{(ij)}$  and  $d\Omega_{(ji)}$  denote the invariant flux, the invariant differential elastic cross-section and the element of solid angle that characterize a binary collision between the particles of constituent  $i$  with those of constituent  $j$ , respectively. The differential  $d^3 v_{(i)}^*$  stands for  $\frac{d^3 v_{(i)}}{v_{(i)}^4}$ , also an invariant. The cross-section  $\sigma_{(ij)}$  has special symmetries [17] that guarantee the existence of inverse collisions such that the principle of microscopic reversibility is satisfied. The quantities  $f_{(i)}$  and  $f'_{(i)}$  denote the distribution functions before and after a collision, respectively.

The collisional invariants in this case are the rest mass of each species  $m_{(i)}$  and the four-momentum  $m_{(i)} v_{(i)}^\alpha$ , where the energy is included in the temporal component  $m_{(i)} v_{(i)}^4$ . In the following subsections, these quantities will be used to obtain balance equations. It is important to notice at this point that the molecular velocity in the previous equations is measured by an observer in an arbitrary frame, which we call laboratory frame.

### A. Particle Number Conservation

By multiplying the Boltzmann equation, Eq. (II.2), by  $m_{(i)}$  and integrating over  $d^3 v_{(i)}^*$  one finds

$$\left( m_{(i)} \int v_{(i)}^\alpha f_{(i)} d^3 v_{(i)}^* \right)_{,\alpha} = 0, \quad (\text{II.4})$$

where

$$N_{(i)}^\alpha = m_{(i)} \int v_{(i)}^\alpha f_{(i)} d^3 v_{(i)}^* \quad (\text{II.5})$$

is the mass four-flux in an arbitrary frame. The barycentric velocity is thus defined as

$$nU^\alpha = \frac{N_{(1)}^\alpha}{m_{(1)}} + \frac{N_{(2)}^\alpha}{m_{(2)}}, \quad (\text{II.6})$$

which is consistent with Eckart's definition for the hydrodynamic four-velocity. Here  $n = n_{(1)} + n_{(2)}$  is the particle number density and represents an invariant. We also define the relativistic diffusive four-flux in the co-moving frame as,

$$J_{(i)}^\alpha = m_{(i)} \int K_{(i)}^\alpha f_{(i)} d^3 K_{(i)}^*, \quad (\text{II.7})$$

where  $K_{(i)}^\alpha$  is the four-velocity of the particles of the species  $i$  measured in the co-moving frame, i.e.  $K_{(i)}^\alpha$  is the chaotic or thermal velocity [18–20]. Then  $N_{(i)}^\alpha$  and  $J_{(i)}^\beta$  are related by a Lorentz transformation as follows,

$$N_{(i)}^\alpha = \mathcal{L}_\beta^\alpha J_{(i)}^\beta, \quad (\text{II.8})$$

where  $\mathcal{L}_\beta^\alpha$  is the transformation from the co-moving frame, where  $U^m = 0$ , to an arbitrary one moving with a four-velocity  $U^\alpha$ .

With the help of these equations, one can find the complete particle number conservation equation, see Ref. [21]. In this work we only need them at Euler’s level, because we will use the Chapman and Enskog method up to first order in the gradients. Thus, we have that,

$$n_{(i)} U_{,\alpha}^\alpha + U^\alpha n_{(i),\alpha} = 0. \quad (\text{II.9})$$

for the particle number conservation.

## B. Momentum and Energy Balance

In order to obtain the energy-momentum balance for the mixture, Boltzmann’s equation is now multiplied by  $m_{(i)} v_{(i)}^\alpha$  and integrated over  $d^3 v_{(i)}^*$ , which yields

$$T_{,\alpha}^{\beta\alpha} = \left( T_{(1)}^{\beta\alpha} + T_{(2)}^{\beta\alpha} \right)_{,\alpha} = 0, \quad (\text{II.10})$$

where

$$T^{\beta\alpha} = \sum_i m_{(i)} \int v_{(i)}^\beta v_{(i)}^\alpha f_{(i)} d^3 v_{(i)}^*. \quad (\text{II.11})$$

In order to establish the form of the tensor  $T^{\beta\alpha}$  we recognize that, as defined in Eq. (II.11), it is referred to an arbitrary reference frame. Thus, we can express it in terms of  $\tilde{T}^{\gamma\phi}$ , measured in the co-moving frame defined above, as

$$T^{\beta\alpha} = \mathcal{L}_\gamma^\beta \mathcal{L}_\phi^\alpha \tilde{T}^{\gamma\phi}, \quad (\text{II.12})$$

where again,  $\mathcal{L}_\phi^\alpha$  and  $\mathcal{L}_\gamma^\beta$  are the Lorentz transformations from the co-moving frame to an arbitrary one moving with a four-velocity  $U^\alpha$ . Following S. Weinberg [22] and using the fact that the stress-energy tensor is symmetric (see Eq. (II.11)), we assume that in the co-moving frame it has the

form,

$$\tilde{T}^{\beta\alpha} \doteq \begin{pmatrix} p & 0 & 0 & 0 \\ 0 & p & 0 & 0 \\ 0 & 0 & p & 0 \\ 0 & 0 & 0 & ne \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & q^1 \\ 0 & 0 & 0 & q^2 \\ 0 & 0 & 0 & q^3 \\ q^1 & q^2 & q^3 & 0 \end{pmatrix} + \begin{pmatrix} \pi^{11} & \pi^{12} & \pi^{13} & 0 \\ \pi^{12} & \pi^{22} & \pi^{23} & 0 \\ \pi^{13} & \pi^{23} & \pi^{33} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (\text{II.13})$$

In Eq. (II.13) we have separated the proper equilibrium quantities namely, the hydrostatic pressure

$$p = \frac{1}{3} \tilde{T}^{mm}, \quad (\text{II.14})$$

and the energy density per particle

$$ne = \tilde{T}^{44}. \quad (\text{II.15})$$

On the other hand, the non equilibrium quantities are

$$q^m = c\tilde{T}^{4m} = c\tilde{T}^{m4} \quad (\text{II.16})$$

for the heat flux and

$$\Pi^{mn} = \tilde{T}^{mn}, \quad (\text{II.17})$$

for the Navier tensor. Introducing Eq. (II.13) in Eq.(II.12) yields

$$T^{\alpha\beta} = pg^{\alpha\beta} + \frac{1}{c^2} (p + ne) U^\alpha U^\beta + \frac{1}{c^2} (U^\alpha \mathcal{L}_\mu^\beta q^\mu + U^\beta \mathcal{L}_\mu^\alpha q^\mu) + \mathcal{L}_\mu^\beta \mathcal{L}_\nu^\alpha \Pi^{\mu\nu}, \quad (\text{II.18})$$

where  $g^{\alpha\beta}$  is the metric tensor. In Eq. (II.18) we identify the first two terms as the relativistic energy-momentum tensor at Euler's level. The third and fourth terms represent the non-equilibrium generalization with the heat and viscous dissipation terms as found from kinetic theory grounds for the single fluid in Ref [9].

We now calculate the derivative in Eq. (II.10) using Eq. (II.18) and its projection with the four-velocity namely,  $U_\mu T^{\mu\nu}_{,\nu}$ . Neglecting all the terms which contain corrections whose order is beyond Euler's regime [21], and after laborious calculations one finds:

$$\tilde{\rho} \dot{U}^\beta + h^{\beta\nu} p_{,\nu} = 0, \quad (\text{II.19})$$

and

$$n\dot{e} = -pU^\mu_{,\mu}, \quad (\text{II.20})$$

where Eqs. (II.19) and (II.20) are the momentum and internal energy balance equations respectively. Here,

$$\tilde{\rho} = \sum_i m_{(i)} n_{(i)} G(z_{(i)}) = \tilde{\rho}_{(1)} + \tilde{\rho}_{(2)}, \quad (\text{II.21})$$

and

$$G(z_{(i)}) = \frac{\mathcal{K}_3\left(\frac{1}{z_{(i)}}\right)}{\mathcal{K}_2\left(\frac{1}{z_{(i)}}\right)}, \quad (\text{II.22})$$

with  $z_{(i)} = \frac{kT}{m_{(i)}c^2}$  being the well-known relativistic parameter. The dot denotes a proper time derivative and is defined as  $\dot{(\cdot)} = U^\mu (\cdot)_{,\mu}$ .

Equation (II.20) is related to the temperature evolution by assuming that the internal energy density depends only on the temperature  $e = C_v T$ . The details of the calculations above can be found in Refs. [9, 21].

### III. LINEARIZATION OF THE BOLTZMANN EQUATION

In this section we proceed to apply the well-known Chapman-Enskog method to linearize the covariant form of Boltzmann's equation. Following the ideas in Ref. [9], we will perform all calculations in the co-moving frame such that Eq. (II.2) now reads,

$$K_{(i)}^\alpha f_{(i),\alpha} = \sum_{j=1}^2 J_{(ij)}, \quad (\text{III.1})$$

where  $K_{(i)}^\alpha$  is the four-velocity measured in such frame. As usual, we now assume that the distribution functions  $f_{(i)}(x^\alpha, K_{(i)}^\alpha, t)$  can be taken as functionals of the locally conserved variables namely  $f_{(i)}(x^\alpha, K_{(i)}^\alpha | n_{(i)}, U^\alpha, T)$ , and further, they may be expanded in power series of a inhomogeneity parameter around the local equilibrium distribution function  $f_{(i)}^{(0)}$  defined in an arbitrary frame as [23–25],

$$f_{(i)}^{(0)} = \frac{n_{(i)}}{4\pi c^3 z_{(i)} \mathcal{K}_2\left(\frac{1}{z_{(i)}}\right)} \exp\left(\frac{U^\beta v_{(i)\beta}}{z_{(i)} c^2}\right), \quad (\text{III.2})$$

which in the co-moving frame reduces to,

$$f_{(i)}^{(0)} = \frac{n_{(i)}}{4\pi c^3 z_{(i)} \mathcal{K}_2\left(\frac{1}{z_{(i)}}\right)} \exp\left(-\frac{\gamma k_{(i)}}{z_{(i)}}\right), \quad (\text{III.3})$$

where  $\gamma_{k(i)} = \left(1 - k_{(i)}^2/c^2\right)^{-1/2}$  is the usual Lorentz factor and  $k_{(i)}^2$  is the magnitude of the chaotic or thermal velocity. Omitting unnecessary arguments, we resort to the linear theory [26] and expand Eq. (III.1) as

$$f_{(i)} = f_{(i)}^{(0)} (1 + \phi_{(i)}) . \quad (\text{III.4})$$

Substitution of Eq. (III.4) into (III.1) with the help of the functional hypothesis and the Eqs. (II.9), (II.19) and (II.20), leads to

$$K_{(i)}^m \left\{ -\gamma_{k(i)} \frac{1}{z_{(i)} c^2 \tilde{\rho}} p_{,m} + (\ln n_{(i)})_{,m} + \left[ 1 + \frac{1}{z_{(i)}} \left( \gamma_{k(i)} - G(z_{(i)}) \right) \right] (\ln T)_{,m} \right\} = [C(\phi_{(i)}) + C(\phi_{(i)} + \phi_{(j)})] . \quad (\text{III.5})$$

Notice that in Eq. (III.5) we have omitted the second rank tensorial terms since Curie's principle establishes that in isotropic systems only forces and fluxes of the same tensorial rank couple among themselves. Clearly, there is an equation similar to Eq. (III.5) for species  $j$ . The linearized collision kernel now reads

$$C(\phi_{(i)} + \phi_{(j)}) = \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} (\phi_{(j)}' + \phi_{(i)}' - \phi_{(j)} - \phi_{(i)}) F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 v_{(j)}^* , \quad (\text{III.6})$$

and,

$$C(\phi_{(i)}) = \int \cdots \int f_{(i)}^{(0)} f_{(i)}^{(0)} (\phi_{(i)}' + \phi_{(i)}' - \phi_{(i)} - \phi_{(i)}) F_{(ii)} \sigma_{(ii)} d\Omega_{(ii)} d^3 v_{(i)}^* .$$

The left hand side of Eq. (III.5) contains terms involving gradients of the intensive thermodynamical variables,  $p_{,m}$ ,  $(n_{(i)})_{,m}$  and  $T_{,m}$ , which we identify with thermodynamic forces. The question that arises is how to select among them, a representation in which Onsager's reciprocity relations hopefully turn out to be valid. This will be discussed in the following sections.

#### IV. SOLUTION WITH TWO THERMODYNAMIC FORCES

Following the statement issued above, we will proceed to discuss the aforementioned representations. For instance, we first re-arrange the left hand side of Eq. (III.5) to read as,

$$K_{(i)}^m \left\{ [d_{m(ij)}] + \frac{1}{z_{(i)}} \left( \gamma_{k(i)} - G(z_{(i)}) \right) \left[ \frac{T_{,m}}{T} - \frac{1}{nh_E} p_{,m} \right] \right\} = [C(\phi_{(i)}) + C(\phi_{(i)} + \phi_{(j)})] , \quad (\text{IV.1})$$



where

$$d_{m(ij)} = n_{(j)} \left( \frac{m_{(j)} G(z_{(j)}) - m_{(i)} G(z_{(i)})}{\tilde{\rho}} \right) \frac{p_{,m}}{p} + \frac{n}{n_{(i)}} (n_{i0})_{,m}, \quad (\text{IV.2})$$

and using the notation  $nh_E = \tilde{\rho}c^2$ , and  $n_{i0} = \frac{n_{(i)}}{n}$  representing an invariant. This choice implies that we are considering two vector forces in the system namely,

$$d_{m(ij)} \quad \text{and} \quad \frac{T_{,m}}{T} - \frac{1}{nh_E} p_{,m}. \quad (\text{IV.3})$$

The second term may be regarded as related to a generalized Fourier's equation with a thermal force that includes both a temperature and pressure gradients [7]. Further it may be shown that in the non-relativistic limit, the coefficient of such force in Eq. (IV.1) reduces to,

$$\frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) \rightarrow \frac{m_{(i)} k_{(i)}^2}{2k_B T} - \frac{5}{2}, \quad (\text{IV.4})$$

and the coefficient of the pressure gradient vanishes because  $\left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) \rightarrow 0$ . Thus, the inhomogeneous term in Eq. (III.5) reduces to the well-known expression of the classical linearized Boltzmann equation.

On the other hand  $d_{m(ij)} = -d_{m(ji)} \equiv d_m$  may be considered as a generalization of the standard diffusive force to a relativistic scheme, since indeed, in the non relativist case Eq. (IV.2) reduces to,

$$d_{m(ij)} \rightarrow \frac{n_{(j)}}{\rho p} (m_{(j)} - m_{(i)}) \nabla p + \frac{n}{n_{(i)}} \nabla n_{i0}, \quad (\text{IV.5})$$

which is in accordance with phenomenological [28] and kinetic [29] classical expressions.

Having selected the above thermodynamic forces, the solution to Eq. (IV.1) reads as [30, 31],

$$\phi_{(i)} = -K_{(i)}^m A_{(i)} \left[ \frac{T_{,m}}{T} - \frac{1}{nh_E} p_{,m} \right] - \sum_i K_{(i)}^m D_{(i)} d_m. \quad (\text{IV.6})$$

Substitution of Eq. (IV.6) in (IV.1) leads to two independent equations for the scalar functions  $A_{(i)}$  and  $D_{(i)}$ , namely,

$$K_{(i)}^m = - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m ' D_{(j)} ' + K_{(i)}^m ' D_{(i)} ' - K_{(j)}^m D_{(j)} - K_{(i)}^m D_{(i)} \right] F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^*, \quad (\text{IV.7})$$

$$K_{(i)}^m \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) = - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m A_{(j)} + K_{(i)}^m A_{(i)} - K_{(j)}^m A_{(j)} - K_{(i)}^m A_{(i)} \right] F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^*, \quad (\text{IV.8})$$

We will now use the expressions for the mass and energy fluxes arising in this representation to prove the validity of Onsager's reciprocity relations in this scheme. The diffusive mass flux has been defined in Eq. (II.7), which with the help of Eq. (IV.6) and (III.4) can be written as follows,

$$\frac{J_{(i)}^m}{m_{(i)}} = -\frac{1}{3} \int f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} A_{(i)} d^3 K_{(i)}^* \left[ \frac{T^{,m}}{T} - \frac{1}{nh_E} p^{,m} \right] - \frac{1}{3} \int f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} D_{(i)} d^3 K_{(i)}^* d^m, \quad (\text{IV.9})$$

In Eq. (IV.9) the transport coefficients are identified as,

$$\frac{J_{(i)}^m}{m_{(i)}} = -L_{dq} \left[ \frac{T^{,m}}{T} - \frac{1}{nh_E} p^{,m} \right] - L_{dd} d^m, \quad (\text{IV.10})$$

where  $L_{dq}$  and  $L_{dd}$  are the integrals appearing in Eq. (IV.9).

For the energy flux we propose the form which is given in the literature [28],

$$\frac{q_{tot}^m}{kT} = \frac{1}{kT} \sum_i (q_{(i)}^m - h_{(i)} J_{(i)}^m), \quad (\text{IV.11})$$

where

$$h_{(i)} = \frac{kT}{z_{(i)}} G(z_{(i)}), \quad (\text{IV.12})$$

is the enthalpy [6]. After Eqs. (II.16) and (II.7) are introduced in Eq. (IV.11) one obtains,

$$\frac{q_{tot}^m}{kT} = -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{(i)}^n K_{n(i)} A_{(i)} d^3 K_{(i)}^* \left[ \frac{T^{,m}}{T} - \frac{1}{nh_E} p^{,m} \right] \quad (\text{IV.13})$$

$$- \frac{1}{3} \sum_i \int f_{(i)}^{(0)} \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{(i)}^n K_{n(i)} D_{(i)} d^3 K_{(i)}^* d^m, \quad (\text{IV.14})$$

or

$$\frac{q_{tot}^m}{kT} = -L_{qq} \left[ \frac{T^{,m}}{T} - \frac{1}{nh_E} p^{,m} \right] - L_{qd} d^m. \quad (\text{IV.15})$$

Equations (IV.10) and (IV.15) are now in a form which, by a similar analysis as the one performed in the classical case (see Ref. [29]) are bound to lead to the required relations of symmetry.

To show this we start by constructing an ‘‘Onsagerian’’ matrix, namely,

$$\begin{pmatrix} q_{tot}^m \\ J_{(i)}^m \end{pmatrix} = - \begin{pmatrix} L_{qq} & L_{qd} \\ L_{dq} & L_{dd} \end{pmatrix} \begin{pmatrix} \frac{T^{,m}}{T} - \frac{1}{nh_E} p^{,m} \\ d^m \end{pmatrix}. \quad (\text{IV.16})$$

Then, one proceeds by multiplying both sides of Eq. (IV.7) by  $K_{(i)m}A_{(i)}$  and integrating over  $d^3K_{(i)}^*$  to obtain the form

$$\begin{aligned} & \int \frac{1}{3} \left( K_{(i)}^n K_{n(i)} \right) A_{(i)} d^3 K_{(i)}^* \\ &= - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m ' D_{(j)} ' + K_{(i)}^m ' D_{(i)} ' - K_{(j)}^m D_{(j)} - K_{(i)}^m D_{(i)} \right] K_{(i)m} A_i F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^* d^3 K_{(i)}^* \\ & \equiv \{D, A\}. \end{aligned} \tag{IV.17}$$

On the other hand, multiplying Eq. (IV.8) by  $K_{(i)m}D_{(i)}$  and integrating over  $dK_{(i)}^*$  yields

$$\begin{aligned} & \int \frac{1}{3} \left( K_{(i)}^n K_{n(i)} \right) \frac{1}{z_{(i)}} \left( \gamma_{k(i)} - G(z_{(i)}) \right) D_{(i)} d^3 K_{(i)}^* \\ &= - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m ' A_{(j)} ' + K_{(i)}^m ' A_{(i)} ' - K_{(j)}^m A_{(j)} - K_{(i)}^m A_{(i)} \right] K_{(i)m} D_{(i)} F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^* d^3 K_{(i)}^* \\ & \equiv \{A, D\}. \end{aligned} \tag{IV.18}$$

Equations (IV.17) and (IV.18) may be symmetrized by taking into account the invariance of  $F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^* d^3 K_{(i)}^*$  (see Ref. [7]), and using the same symmetry arguments as in the conventional proof of the H-theorem. Such a procedure leads to

$$\{A, D\} = \{D, A\}, \tag{IV.19}$$

and thus

$$L_{dq} = L_{qd}. \tag{IV.20}$$

Emphasis should be made on the fact that we verified the reciprocity of the Onsager relations using the standard kinetic definition for two fluxes but not for the forces. In this section, we are assuming that the generalization for the Fourier's equation has the form given by Eq. (IV.15). Here  $p^m$  is considered as part of this force in order to obtain integral equations in which the transformation of their kernels fulfill the symmetry requirements. Thus in this representation one cannot speak of the canonical forms of the Dufour-Soret effects that relate the diffusion coefficients to *strictly the thermal conductivity*.

However, in the following section we will overcome this difficulty by introducing a volumetric flow which arises solely from the fact that in the theory of relativity volumes are not invariants. This representation is completely new and bears some resemblance with recent work by H. Brenner [11–13], who argues that this kind of fluxes are important in non-relativistic fluids.

## V. SOLUTION WITH THREE THERMODYNAMIC FORCES

In this section we explore the possibility of a third thermodynamic flux in the system. The motivation behind such task is the interest to explore the possibility of keeping the temperature and pressure gradients as independent forces which would yield a Fourier-type constitutive equation for the heat flux relating it exclusively to a temperature gradient. This will imply that the heat flux caused by a pressure gradient constitutes a cross effect. This is a purely relativistic effect and we shall see how it relates to with the pressure, or density, gradient term that arises in the case of the high temperature in a one component gas.

To achieve this new representation we start by re-arranging Eq. (III.5) as follows,

$$K_{(i)}^m \left\{ d_m + \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) \frac{T_{,m}}{T} - \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) \left[ \frac{n_{(i)} m_{(i)} p_{,m}}{\tilde{\rho} p_{(i)}} \right] \right\} = [C(\phi_{(i)}) + C(\phi_{(i)} + \phi_{(j)})] \quad (\text{V.1})$$

for species  $i$ , recalling that there is a similar equation for species  $j$ . Notice that we are considering a new force,

$$V_{(i)m} \equiv \frac{n_{(i)} m_{(i)} p_{,m}}{\tilde{\rho} p_{(i)}},$$

which satisfies

$$V_{(1)m} = \frac{m_{(1)}}{m_{(2)}} V_{(2)m} \equiv V_m. \quad (\text{V.2})$$

Equation (V.1) leads to a solution of the form

$$\phi_{(i)} = -K_{(i)}^m A_{(i)} \frac{T_{,m}}{T} - \sum_j K_{(j)}^m B_{(j)} V_m - \sum_j K_{(j)}^m D_{(j)} d_m. \quad (\text{V.3})$$

Substitution of Eq. (V.3) into (V.1) yields three independent equations, namely,

$$K_{(i)}^m \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) = [C(K_{(i)}^m A_{(i)}) + C(K_{(i)}^m A_{(i)} + K_{(j)}^m A_{(j)})], \quad (\text{V.4})$$

$$K_{(i)}^m \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) = [C(K_{(i)}^m B_{(i)}) + C(K_{(i)}^m B_{(i)} + K_{(j)}^m B_{(j)})], \quad (\text{V.5})$$

$$K_{(i)}^m = [C(K_{(i)}^m D_{(i)}) + C(K_{(i)}^m D_{(i)} + K_{(j)}^m D_{(j)})]. \quad (\text{V.6})$$

Equation (V.5) is now the new ingredient in this representation. To understand its physical meaning we proceed as follows. Consider the motion of an individual particle which collides with

another one. After the collision it will travel a length  $\lambda$ , the mean free path, before colliding with a third one. Recall also that the mean free time is much greater than the collision time. One can thus construct a sphere centered in the particle (in general it can be any other geometric figure) with volume  $V = \frac{4}{3}\pi\lambda^3$  that, when the speed of the particle is comparable with the speed of light, by Lorentz's contraction, is deformed into a ellipsoid with volume  $\frac{4}{3}\pi\lambda^3\gamma_k$ . Therefore, in the relativistic case, an observer sees a change in this volume with a privileged direction  $\vec{k}$ . This is the process which gives rise to "volume or volumetric flow" and a system with an apparently additional state variable. In order to explore its significance we establish the transport equation characterizing its flow. In the case of a binary mixture by multiplying Boltzmann's equation by the microscopic change in the volume  $a\gamma_{k(i)}$  where  $a$  is a constant, and integrating over the velocities  $d^3K_{(i)}^*$  yields,

$$\left( \int \gamma_{k(i)} K_{(i)}^\alpha f_{(i)} d^3 K_{(i)}^* \right)_{,\alpha} = \int \gamma_{k(i)} (J_{(ii)} + J_{(ij)}) d^3 K_{(i)}^* \quad (V.7)$$

$$= \pi_{vol}$$

which is a balance equation for the change in the volume in the gas. Notice that in the non-relativistic limit, the right hand side vanishes, implying that there is no such change in volume. The physical implications of this flux are further discussed in the final section.

In the case of mixtures, the energy flux corresponding to heat dissipation to be considered in Onsager's formalism is constructed by subtracting the diffusive mass flux times the enthalpy from the heat flux [28, 32]. In a similar fashion, we define the total volume (adimensional) flux as,

$$J_V^m = \sum_i \left( \int \gamma_{k(i)} K_{(i)}^m f_{(i)} d^3 K_{(i)}^* - \frac{h_{E(i)}}{m_{(i)} c^2} \frac{J_{(i)}^m}{m_{(i)}} \right), \quad (V.8)$$

where  $n_{(i)} h_{E(i)} = c^2 \tilde{\rho}_{(i)}$ . Thus, using Eqs. (V.3) and (III.4) we have that,

$$\begin{aligned} J_V^m = & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \left( \gamma_{k(i)} - G(z_{(i)}) \right) K_{(i)}^n K_{(i)n} A_{(i)} d^3 K_{(i)}^* \frac{T^{,m}}{T} \\ & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \left( \gamma_{k_i} - G(z_{(i)}) \right) K_{(i)}^n K_{(i)n} B_{(i)} d^3 K_{(i)}^* V^m \\ & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \left( \gamma_{k(i)} - G(z_{(i)}) \right) K_{(i)}^n K_{(i)n} D_{(i)} d^3 K_{(i)}^* d^m \end{aligned} \quad (V.9)$$

or

$$J_V^m = -L_{Vq} \frac{T^{,m}}{T} - L_{VV} V^m - L_{Vd} d^m. \quad (V.10)$$

which introduces two new transport cross-coefficients  $L_{Vq}$ ,  $L_{Vd}$  and one corresponding to the direct effect  $L_{VV}$ .

As mentioned before, the dissipative energy flux is given by

$$\begin{aligned} \frac{q_{tot}^m}{k_B T} = & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{(i)}^n K_{n(i)} A_{(i)} d^3 K_{(i)}^* \frac{T^{,m}}{T} \\ & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{(i)}^n K_{n(i)} B_{(i)} d^3 K_{(i)}^* V^m \\ & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{(i)}^n K_{n(i)} D_{(i)} d^3 K_{(i)}^* d^m \end{aligned} \quad (V.11)$$

or

$$\frac{q_{tot}^m}{k_B T} = -L_{qq} \frac{T^{,m}}{T} - L_{qV} V^m - L_{qd} d^m. \quad (V.12)$$

and for the mass flow we have,

$$\frac{J_{(i)}^m}{m_{(i)}} = -\frac{1}{3} \int f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} A_{(i)} d^3 K_{(i)}^* \frac{T^{,m}}{T} - \frac{1}{3} \int f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} B_{(i)} d^3 K_{(i)}^* V^m - \frac{1}{3} \int f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} D_{(i)} d^3 K_{(i)}^* d^m, \quad (V.13)$$

which can also be written as

$$\frac{J_{(i)}^m}{m_{(i)}} = -L_{dq(i)} \frac{T^{,m}}{T} - L_{dV(i)} V^m - L_{dd(i)} d^m. \quad (V.14)$$

From the previous equations, one can readily identify the Soret and Dufour cross-effects. The verification of the Onsager reciprocity relations will support that these are the correct generalizations for such effects.

Equations (V.10), (V.12) and (V.14) will be explored to see whether they comply with the Onsager reciprocity relations. As before, we construct the Onsagerian matrix,

$$\begin{pmatrix} q_{tot}^m \\ J_{(i)}^m \\ J_V^m \end{pmatrix} = - \begin{pmatrix} L_{qq} & L_{qd} & L_{qV} \\ L_{dq(i)} & L_{dd(i)} & L_{dV(i)} \\ L_{Vq} & L_{Vd} & L_{VV} \end{pmatrix} \begin{pmatrix} \frac{T^{,m}}{T} \\ d_{(i)}^m \\ V^m \end{pmatrix}, \quad (V.15)$$

where we introduced the term  $V^m$  as the direct driving force for the volume flux  $J_V^m$ . Then, by the same procedure and arguments as those in the previous section, we will verify the symmetries

$$L_{dq(i)} \stackrel{?}{=} L_{qd} \quad (V.16)$$

$$L_{Vq} \stackrel{?}{=} L_{qV} \quad (\text{V.17})$$

$$L_{Vd} \stackrel{?}{=} L_{dV(i)}. \quad (\text{V.18})$$

First, for Eq. (V.16), Eqs. (V.4) and (V.6) are multiplied by  $K_{(i)}^m D_{(i)}$  and  $K_{(i)}^m A_{(i)}$  respectively. After integration over  $d^3 K_{(i)}^*$  one finds,

$$\begin{aligned} & \int K_{(i)}^n \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{n(i)} D_{(i)} dK_{(i)}^* \\ &= - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m ' A_{(j)} ' + K_{(i)}^m ' A_{(i)} ' - K_{(j)}^m A_{(j)} - K_{(i)}^m A_{(i)} \right] K_{(i)}^m D_{(i)} F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^* d^3 K_{(i)}^* \\ & \equiv \{A, D\}, \end{aligned} \quad (\text{V.19})$$

or

$$\begin{aligned} & \int K_{(i)}^n K_{n(i)} A_{(i)} dK_{(i)}^* \\ &= - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m ' D_{(j)} ' + K_{(i)}^m ' D_{(i)} ' - K_{(j)}^m D_{(j)} - K_{(i)}^m D_{(i)} \right] K_{(i)m} A_{(i)} F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^* d^3 K_{(i)}^* \\ & \equiv \{D, A\} \end{aligned} \quad (\text{V.20})$$

where, by the symmetry properties of the collisional term,  $\{A, D\} = \{D, A\}$ , implying that Eq. (V.16) holds. Secondly, multiplying Eqs. (V.4) and (V.5) by  $K_{(i)}^m B_{(i)}$  and  $K_{(i)}^m A_{(i)}$  respectively, and integrating over  $d^3 K_{(i)}^*$  yields,

$$\begin{aligned} & \int K_{(i)}^n \frac{1}{z_{(i)}} \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{n(i)} B_{(i)} dK_{(i)}^* \\ &= - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m ' A_{(j)} ' + K_{(i)}^m ' A_{(i)} ' - K_{(j)}^m A_{(j)} - K_{(i)}^m A_{(i)} \right] K_{m(i)} B_{(i)} F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^* d^3 K_{(i)}^*, \\ & \equiv \{A, B\} \end{aligned} \quad (\text{V.21})$$

or

$$\begin{aligned} & \int K_{(i)}^n \left( \gamma_{k_{(i)}} - G(z_{(i)}) \right) K_{n(i)} A_{(i)} dK_{(i)}^* \\ &= - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m ' B_{(j)} ' + K_{(i)}^m ' B_{(i)} ' - K_{(j)}^m B_{(j)} - K_{(i)}^m B_{(i)} \right] K_{m(i)} A_{(i)} F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^* d^3 K_{(i)}^*, \\ & \equiv \{B, A\} \end{aligned} \quad (\text{V.22})$$

and since  $\{A, D\} = \{B, A\}$ , Eq. (V.17) holds. Lastly, Eqs. (V.5) and (V.6) are multiplied by

$K_{(i)}^m D_{(i)}$  and  $K_{(i)}^m B_{(i)}$  respectively, yielding,

$$\begin{aligned} & \int K_{(i)}^n \left( \gamma_{k(i)} - G(z_{(i)}) \right) K_{n(i)} D_{(i)} d^3 K_{(i)}^* \\ &= - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m \cdot B_{(j)} \cdot + K_{(i)}^m \cdot B_{(i)} \cdot - K_{(j)}^m B_{(j)} - K_{(i)}^m B_{(i)} \right] K_{m(i)} D_{(i)} d^3 K_{(i)}^* \quad (\text{V.23}) \\ & \equiv \{B, D\} \end{aligned}$$

$$\begin{aligned} & \int K_{(i)}^n K_{n(i)} B_{(i)} dK_{(i)}^* \\ &= - \sum_j \int \cdots \int f_{(i)}^{(0)} f_{(j)}^{(0)} \left[ K_{(j)}^m \cdot D_{(j)} \cdot + K_{(i)}^m \cdot D_{(i)} \cdot - K_{(j)}^m D_{(j)} - K_{(i)}^m D_{(i)} \right] K_{(i)m} B_{(i)} F_{(ij)} \sigma_{(ij)} d\Omega_{(ji)} d^3 K_{(j)}^* d^3 K_{(i)}^*, \\ & \equiv \{D, B\} \end{aligned} \quad (\text{V.24})$$

where again,  $\{B, D\} = \{D, B\}$ , justifying Eq. (V.18) .

At this point we have verified that Onsager's symmetries hold in this representation. The authentic Dufour effect corresponds to the transport coefficient  $L_{qd}$ , while the Soret effect is related to  $L_{dq}$ , whose explicit expressions are depicted in Eqs. (V.12) and (V.14). Now, from the Onsagerian matrix we identify two new cross-effects represented by  $L_{dV}$  and  $L_{qV}$ . These effects do not appear in the non-relativistic theory. Curiously enough, they have been proposed in an entirely phenomenological way by several authors in a non-relativistic version of linear irreversible thermodynamics whose origin dates back to the basis of hydrodynamics as formulated by L. Euler in 1755 Ref. [33]. However, the volume flow is defined here by taking into account the non-invariance of an element volume under Lorentz transformations, and vanishes in the non-relativistic limit. In the classical framework mentioned above, its origin is entirely different [12].

The Onsager reciprocity relations are not necessarily fulfilled in other representations. We shall present an example namely, the most common case of the relativistic binary mixture where instead of using  $d^m$  as the thermodynamic force, the gradient of the chemical potential is used. In classical irreversible thermodynamics one often finds that many writers believe that the appropriate thermodynamic forces to describe cross-effects in the case of mixtures are the chemical potentials of the species. For the non-relativistic case, when the mixture is non-isothermal it was clearly shown Ref. [29] that this is incorrect. In such representation the ORR do not hold true. Here we wish to show that the same statement is valid for a non-isothermal binary mixture of inert gases in special relativity.



To verify this statement we recall that for an ideal gas the chemical potential reads as,

$$\mu_{(i)} = \frac{k_B T}{m_{(i)}} \left( \ln n_{(i)} - \frac{3}{2} \ln \alpha(T) \right), \quad (\text{V.25})$$

where  $\alpha(T)$  is a function related to the Jüttner distribution which is irrelevant to the present calculation. Whence,

$$(\nabla \mu_{(i)})_T = z_{(i)} c^2 \frac{\nabla n_{(i)}}{n_{(i)}}, \quad (\text{V.26})$$

where  $(\nabla \mu_{(i)})_T$  is the gradient of the chemical potential for species  $i$  at constant temperature. Further Eq. (IV.2) can be rewritten by using the equation of state  $p = nk_B T$  as

$$d^m = \frac{n_{(j)}}{\tilde{\rho}} (m_{(j)} G(z_{(j)}) - m_{(i)} G(z_{(i)})) \frac{T^m}{T} + \frac{n_{(j)}}{\tilde{\rho}} \left( m_{(j)} G(z_{(j)}) \frac{n_{(i)}^m}{n_{(i)}} - m_{(i)} G(z_{(i)}) \frac{n_{(j)}^m}{n_{(j)}} \right). \quad (\text{V.27})$$

Substitution of Eq. (V.26) into (V.27), introducing the resulting expression for  $d^m$  in Eqs. (V.10), (V.12) and (V.14) leads to,

$$\begin{aligned} \frac{q_{tot}^m}{k_B T} = & -\frac{1}{3} \sum_i \int \frac{f_{(i)}^{(0)} (\gamma_{k_{(i)}} - G(z_{(i)}))}{z_{(i)}} K_{(i)}^n K_{n(i)} \left( A_{(i)} + D_{(i)} \frac{n_{(j)}}{\tilde{\rho}} (m_{(j)} G(z_{(j)}) - m_{(i)} G(z_{(i)})) \right) d^3 K_{(i)}^* \frac{T^m}{T} \\ & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \frac{1}{z_{(i)}} (\gamma_{k_{(i)}} - G(z_{(i)})) K_{(i)}^n K_{n(i)} B_{(i)} d^3 K_{(i)}^* V^m \\ & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} \frac{1}{z_{(i)}} (\gamma_{k_{(i)}} - G(z_{(i)})) K_{(i)}^n K_{n(i)} D_{(i)} d^3 K_{(i)}^* \frac{1}{n h_E} \left( \frac{\tilde{\rho}_{(j)}}{z_{(i)}} (\nabla \mu_{(i)})_T - \frac{n_{(j)} \tilde{\rho}_{(i)}}{n_{(i)} z_{(j)}} (\nabla \mu_{(j)})_T \right), \end{aligned} \quad (\text{V.28})$$

which can also be written as

$$\frac{q_{tot}^m}{k_B T} = -L_{qq}^* \left[ \frac{T^m}{T} \right] - L_{qV}^* V^m - L_{q\mu}^* \frac{1}{n h_E} \left( \frac{\tilde{\rho}_{(j)}}{z_{(i)}} (\nabla \mu_{(i)})_T - \frac{n_{(j)} \tilde{\rho}_{(i)}}{n_{(i)} z_{(j)}} (\nabla \mu_{(j)})_T \right). \quad (\text{V.29})$$

Similarly the volume flux can be written as,

$$\begin{aligned} J_V^m = & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} (\gamma_{k_{(i)}} - G(z_{(i)})) K_{(i)}^n K_{n(i)} \left( A_{(i)} + D_{(i)} \frac{n_{(j)}}{\tilde{\rho}} (m_{(j)} G(z_{(j)}) - m_{(i)} G(z_{(i)})) \right) d^3 K_{(i)}^* \frac{T^m}{T} \\ & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} (\gamma_{k_{(i)}} - G(z_{(i)})) K_{(i)}^n K_{n(i)} B_{(i)} d^3 K_{(i)}^* V^m \\ & -\frac{1}{3} \sum_i \int f_{(i)}^{(0)} (\gamma_{k_{(i)}} - G(z_{(i)})) K_{(i)}^n K_{n(i)} D_{(i)} d^3 K_{(i)}^* \frac{1}{n h_E} \left( \frac{\tilde{\rho}_{(j)}}{z_{(i)}} (\nabla \mu_{(i)})_T - \frac{n_{(j)} \tilde{\rho}_{(i)}}{n_{(i)} z_{(j)}} (\nabla \mu_{(j)})_T \right), \end{aligned} \quad (\text{V.30})$$

or

$$J_V^m = -L_{Vq}^* \frac{T^m}{T} - L_{VV}^* V^m - L_{V\mu}^* \frac{1}{n h_E} \left( \frac{\tilde{\rho}_{(j)}}{z_{(i)}} (\nabla \mu_{(i)})_T - \frac{n_{(j)} \tilde{\rho}_{(i)}}{n_{(i)} z_{(j)}} (\nabla \mu_{(j)})_T \right). \quad (\text{V.31})$$

And lastly, the mass flux reads

$$\begin{aligned} \frac{J_{(i)}^m}{m_{(i)}} = & -\frac{1}{3} \int \left( f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} A_{(i)} + f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} D_{(i)} \frac{n_{(j)}}{\tilde{\rho}} (m_{(j)} G(z_{(j)}) - m_{(i)} G(z_{(i)})) \right) d^3 K_{(i)}^* \frac{T^{,m}}{T} \\ & -\frac{1}{3} \int f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} B_{(i)} d^3 K_{(i)}^* V^m \\ & -\frac{1}{3} \int f_{(i)}^{(0)} K_{(i)}^n K_{n(i)} D_{(i)} d^3 K_{(i)}^* \frac{1}{nh_E} \left( \frac{\tilde{\rho}_{(j)}}{z_{(i)}} (\nabla \mu_{(i)})_T - \frac{n_{(j)} \tilde{\rho}_{(i)}}{n_{(i)} z_{(j)}} (\nabla \mu_{(j)})_T \right), \end{aligned} \quad (\text{V.32})$$

or

$$\frac{J_{(i)}^m}{m_{(i)}} = -L_{dq}^* \frac{T^{,m}}{T} - L_{dV}^* V^m - L_{d\mu}^* \frac{1}{nh_E} \left( \frac{\tilde{\rho}_{(j)}}{z_{(i)}} (\nabla \mu_{(i)})_T - \frac{n_{(j)} \tilde{\rho}_{(i)}}{n_{(i)} z_{(j)}} (\nabla \mu_{(j)})_T \right). \quad (\text{V.33})$$

In Eqs. (V.29), (V.31) and (V.33), when we examine the integral expressions corresponding to those coefficients subject to exhibit the appropriate symmetry which arises from the same transformations used in the proof of the H theorem as well as the results obtained in the previous section one immediately finds that such symmetry does not hold. Therefore it turns out that,

$$L_{dq}^* \neq L_{q\mu}^*, \quad (\text{V.34})$$

and the same for the others cross-coefficients. Thus, these calculations clearly exhibit the fact that also in the relativistic case, the chemical potentials of the species do not provide an adequate representation in which the ORR are valid.

## VI. DISCUSSION

In this paper we have shown that the introduction of the concept of thermal velocity is equally useful to deal with transport properties of diluted mixtures. In fact, the expression we obtained for the total heat flux  $J_{tot}^m$  is consistent with its expression in the phenomenological theory as well as in the non-relativistic case. Secondly we insist that the new result exhibits the existence of two representations in which the ORR are valid. In the one discussed in section 4, where the forces are those that have been used by other authors Refs. [6, 7] for the simple component gas, is characterized by the fact that “Fourier’s like equation” has to be modified by the presence of a pressure gradient.

In the second case as discussed in section 5, we propose the new idea of the volume flux, which may be introduced without modifying the classical Fourier equation, and also gives rise to the

canonical form for the Dufour and Soret effects related with  $L_{qd}$  and  $L_{dq}$ . This representation is new and provides two new cross effects that are only present in the relativistic case namely,  $L_{qV}$  and  $L_{dV}$ . Indeed, one can immediately see from Eq. (V.5) that this contribution vanishes in the non-relativistic limit.

Notice that the volume flow as introduced in Eq. (V.10) may be regarded as a multiple of the heat flux Eq. (V.12) in the single-fluid limit. As shown in the appendix, the constitutive equation for the heat flux and for the volume flux in this limit coincide. Thus, what in the binary mixture is a cross effect turns into a direct effect with a Fourier type constitutive equation in the single-fluid limit.

The apparently new variable associated with the volume transport has a peculiar thermodynamical meaning. This volume flux with its conjugated force are indeed related with the thermodynamic description of the system and when taken into account, clarify the nature of the transport phenomena in a relativistic mixture. This coupling of the volume flux with a pressure gradient is indeed confirmed when calculating the entropy production of the mixture, which constitutes work in progress and will be published elsewhere.

## Acknowledgments

The authors wish to thank Alfredo Sandoval-Villalbazo for his helpful comments and Universidad Iberoamericana Ciudad de Mexico for hosting part of this work. One of us, V. M. acknowledges CONACyT for financial support under scholarship number 203111.

## Appendix

In this appendix we will take the single-fluid limit from equations for the volume flux and the heat flux. Taking  $m_{(i)} = m_{(j)} = m$ ,  $n_{(i)} = n_{(j)} = n$ , from Eqs. (II.16) and (V.7) we have for the heat flux

$$\frac{q_{tot}^m}{k_B T} = \frac{mc^2}{k_B T} \int \gamma_k K^m f d^3 K^*, \quad (\text{VI.1})$$

and for the volume flux

$$J_V^m = \int \gamma_k K^m f d^3 K^*, \quad (\text{VI.2})$$

thus

$$\frac{q_{tot}^m}{k_B T} = \frac{1}{z} J_V^m. \quad (\text{VI.3})$$

It remains to verify that the transport coefficients satisfy the same relations namely, from Eqs. (V.10) and (V.12) with the fact that  $d^m = 0$ , recalling that  $J_{(i)}^m = J_{(j)}^m = 0$  we get,

$$J_V^m = -L_{Vq} \frac{T^{,m}}{T} - L_{VV} \left[ \frac{nm}{\tilde{\rho}} \frac{p^{,m}}{p} \right] \quad (\text{VI.4})$$

and

$$\frac{q_{tot}^m}{k_B T} = -L_{qq} \frac{T^{,m}}{T} - L_{qV} \left[ \frac{nm}{\tilde{\rho}} \frac{p^{,m}}{p} \right], \quad (\text{VI.5})$$

where

$$L_{Vq} = -\frac{1}{3} \int f^{(0)} (\gamma_k - G(z)) K^n K_n A d^3 K^* \quad (\text{VI.6})$$

$$L_{VV} = -\frac{1}{3} \int f^{(0)} (\gamma_k - G(z)) K^n K_n B d^3 K^* \quad (\text{VI.7})$$

$$L_{qq} = -\frac{1}{3} \int f^{(0)} \frac{1}{z} (\gamma_k - G(z)) K^n K_n A d^3 K^* \quad (\text{VI.8})$$

$$L_{qV} = -\frac{1}{3} \int f^{(0)} \frac{1}{z} (\gamma_k - G(z)) K^n K_n B d^3 K^*. \quad (\text{VI.9})$$

Where again we can immediately see that

$$\frac{q_{tot}^m}{k_B T} = \frac{1}{z} J_V^m. \quad (\text{VI.10})$$

Then, in the single-fluid limit, the volume flux turns out to be a multiple of the heat flux.

- 
- [1] M. H. Thoma, Rev. Mod. Phys. **81** 959-968 (2009)
  - [2] T. Schäfer, D. Teaney, Rep. Prog. Phys. **72** 126001 (2009)
  - [3] G. Aad et al, Phys. Rev. Lett. **105**, 252303 (2010)
  - [4] W. Israel, J. Math. Phys. **4** 1163 (1963)
  - [5] W. Israel and J.M. Stewart, Ann. Phys. **118** (1979)

- [6] S. R. de Groot, W. A. van Leeuwen, Ch. G. van Weert; *Relativistic Kinetic Theory*; North-Holland (1980).
- [7] C. Cercignani, G. M. Kremer; *The Relativistic Boltzmann Equation: Theory and Applications*; Birkhauser Verlag (2002).
- [8] A. Sandoval-Villalbazo, L. S. García-Colín, Phys. A **278**, 428-439 (2000)
- [9] A. L. García-Perciante, A. Sandoval-Villalbazo and L. S. García-Colín, J. Non-equil. Thermodyn. (to be published) 2011, arXiv:1007.2815v1 [gr-qc]
- [10] C. Eckart, J. Phys. Rev. **58**, 919 (1940)
- [11] H. Brenner, Phys. A **389** 1297–1316 (2010)
- [12] H. Brenner, Int. J. Eng. Sci. **47** 902–929 (2009)
- [13] H. Brenner, Phys. A **349** 11–59 (2005)
- [14] L. Onsager, Phys. Rev. **37**, 405 (1931); *ibid* **38** 2265 (1931)
- [15] L. Onsager, Phys. Rev. **91**, 1505 (1953)
- [16] H. B. G. Casimir, Rev. Mod. Phys **17**, 343 (1945)
- [17] Ch. G. van Weert, W. A. van Leeuwen, S. R. de Groot, Physica **69**, 441-457 (1973)
- [18] J. C. Maxwell, Scientific Papers of J. C. Maxwell, *On the dynamical theory of gases*; edited by W. D. Niven, (Dover, New York, 1965)
- [19] R. Clausius, Ann. der Physik. 100, 353-380, (1857)
- [20] S. Brush, *The kind of motion we call Heat*; (North-Holland, Amsterdam, 1986)
- [21] Valdemar Moratto, A. L. García-Perciante, L. S. García-Colín, AIP Conf. Proc. **1312**, 80-88. (2010)
- [22] S. Weinberg, *Gravitation and Cosmology: Principles and Applications of the General Theory of Relativity*; John Wiley & Sons (1972)
- [23] F. Jüttner; Ann. Physik und Chemie **34** 856 (1911)
- [24] G. Chacón, L. Dagdug, H. A. Morales-Técotl, Phys. Rev. E **81**, 021126 (2010)
- [25] D. Cubero, J. Casado-Pascual, J. Dunkel, P. Talkner, P. Hänggi, Phys. Rev. Lett. **99**, 170601 (2007)
- [26] S. Chapman y T.G. Cowling; *The mathematical theory of non uniform Gases*; 3 Ed, Cambridge University Press (1970).
- [27] G. M. Kremer (private communication).
- [28] S.R. Groot de, P. Mazur; *Non-equilibrium Thermodynamics*; Dover Publications, Mineola, N.Y.,

(1984)

- [29] P. Goldstein, L.S. García-Colín, J. Non Equilib. Thermodyn. **30**, 173-186 (2005)
- [30] A. L. García-Perciante, A. Sandoval-Villalazo, L. S. García-Colín, Phys A **387** 5073–5079 (2008)
- [31] J.O. Hirschfelder, C.F. Curtis y R.B. Bird, *Molecular theory of gases and liquids*; New York: Wiley, (1954)
- [32] B. C. Eu, *Kinetic Theory and Irreversible Thermodynamics*; John Wiley & Sons, Inc. (1992)
- [33] L. Euler, *Foundations of Differential Calculus, with Applications to Finite Analysis and Series*; Academia imperialis scientiarum Petropolitana, Berolini: Michaelis. (1755)